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AIR PURITY IN DIVING FROM SUBMARINES 1. REVIEW AND PRELIMINARY ANALYSES

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TECHNICAL REVIEW AND APPROVAL

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The experiments reported herein were conducted according to the principles set forth in the current edition of the "Guide for the Care and Use of Laboratory Animals," Institute of Laboratory Animal Resources, National Research Council.

This technical report has been reviewed by the NMRI scientific and public affairs staff and is approved for publication. It is releasable to the National Technical Information Service where it will be available to the general public, including foreign nations.

LARRY W. LAUGHLIN
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Commanding Officer

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INTRODUCTION

The need for divers to use compressed air from submarine air banks raises special problems concerning air purity. Submarine service air banks contain a mixture of "fresh" and interior submarine air. Logistical problems prevent dedication of a large air storage facility exclusively for divers use. Service air banks are used for many routine (e.g., pneumatic control systems) and emergency submarine functions, and submarine interior air is frequently compressed back into the bank which will cycle from about 4000 to 4500 psi. The reuse of service bank air can continue without fresh air replenishment for periods of a month or longer.

Submarine crews breathe the interior air for long periods, so why the concern for divers? First, the processes of compression (by multi-stage oil lubricated compressors), drying, storage, and decompression can potentially add, subtract or modify contaminants in the air. Second, since the air in diving is compressed, the partial pressure - and presumably the toxicity of any contaminants - will increase by breathing the air at a higher pressure. For example, a diver at 99 feet of sea water (fsw), 4 atmospheres absolute (ATA), has a fourfold increase in all gas partial pressures over the exposure for submariners. Thus, the diver is at an increased toxic risk. This is especially worrisome for central nervous system (CNS) depressants since diving is usually done by men working alone using little verbal communication. Systems such as decrements in mental performance that would otherwise be noticeable to companions can be fatal to divers. Finally, the need to monitor (by instruments at about 1 ATA) for accepted toxic limits (at $\frac{1}{4}$ the concentration for the 4 ATA example) requires higher sensitivity in any chemical analysis.

History

Prior to nuclear powered submarines, air quality limited submergence duration by problems of oxygen storage, carbon dioxide accumulation, and battery emissions of chlorine and hydrogen. In the period 1959-1970, a major program was undertaken at the Naval Research Laboratory (NRL) to extend the

closed-boat duration of nuclear submarine atmospheres to a month or longer. Problems and solutions are documented in a series of NRL "annual" reports (1,4,12,14,20-22). A good summary of work through this period is Saalfeld and Saunders (26). The results were procedures and equipment (17) which allowed extended closed-boat operation with only rare serious atmosphere emergencies. Other countries operating diesel powered submarines encounter even more difficult problems, for example with diesel exhaust (11).

Extended submarine operations require an electrically-powered, self-sufficient life-support system. Oxygen is generated by sea water electrolysis with backup of chlorate candles. Carbon dioxide is scrubbed from the air with regenerable monoethanolamine solution with LiOH pellets as a backup adsorbent. Hydrogen and carbon monoxide are eliminated by catalytic oxidation on hopcalite followed by effluent scrubbing with lithium carbonate to remove any acids formed. The catalytic burner operates at 600 °F and is quite efficient for removing many hydrocarbons as well. In addition, large beds of charcoal adsorbent purge the air of many trace contaminants.

Throughout the 1960's, intensive work on submarine atmospheres focused on making old technology more reliable and developing new instrumentation. Methods including gas chromatography and infrared spectrophotometry were explored to measure trace gases at sea. These instruments failed due to reliability problems, and the inability of sailors to operate and maintain the instruments. Eventually, the Central Atmospheric Monitoring System (CAMS-I) was installed on all nuclear submarines. This reliable instrument uses nondispersive infrared detection of CO, and a fixed-collector magnetic mass spectrometer for O₂, CO₂, N₂, H₂, H₂O, R-114 or R-11, and R-12 (5). The CAMS-II, which has a scanning mass spectrometer controlled by a microprocessor (27) is currently undergoing sea trials. Back-up analysis is provided by a paramagnetic O₂ analyzer, a volumetric caustic CO₂ device, and a number of chemical-indicator detector tubes (see below). Recently entering distribution is a portable photoionization detector with broad-range sensitivity to hydrocarbons (32).

Submarine Atmosphere Content

The major constituents of air are not a problem for diving. The submarine starts with "fresh" air at 20.9% O₂, 78.1% N₂, 0.03% CO₂, 0.9% Ar, and no other compound as high as 50 parts per million (ppm). Argon is not monitored or controlled, but field studies have shown that it scarcely varied during a patrol (27). Even during the closed-boat operation, the O₂ is kept close to its starting value. The Submarine Atmosphere Control Manual requires that PO₂ be maintained between 140 and 160 mmHg (18.4 to 21.1% of a standard atmosphere) (17). Since total pressure is required to stay in the range of 700-800 mmHg, the N₂ content remains near 80% of 1 atmosphere. Recent proposals to lower the O₂ content slightly and raise total pressure (11) still would leave sufficient O₂ for compressed gas diving.¹

The greatest problem is carbon dioxide. A crew of 100-150 men generates over 10 pounds per hour. This longstanding problem with submarines has been addressed by one or two regenerative scrubbers that allows CO₂ usually to be kept below the mandated level of 0.8% (8000 ppm) (17). That level represents an engineering compromise of serving a distributed source of CO₂ emission (the crew) with reasonably sized scrubbers and efficient ventilation (usually <5 min turnover time by blowers). However, the maximum allowable CO₂ of 0.8% can be compressed for divers on a 165 fsw dive (6 ATA) to 4.8%; a level that is both hazardous and normally prohibited for diving (18). It is therefore obvious that submarine air cannot be used by divers without a check of the CO₂ level.

The concentrations of all other contaminant gases are far below the levels of O₂, CO₂, Ar and N₂. Carbon monoxide is usually present in the atmosphere despite the catalytic burner. Common sources are cigarette smoking by crew members, food cooking, offgassing of materials, endogenous production, and fire (10,23). Levels of CO also vary drastically in place and time. In

¹Operation at the high pressure and low O₂ corner of this envelope may create an atmosphere rich enough in N₂ to adversely affect the decompression requirement of divers using the air. The decompression problem is outside the scope of this report.

an examination of 9 submarine patrol logs, an average of 7 ppm of CO was found, along with high values of 20 ppm (2).

Because a ship is basically an industrial plant, many other compounds are present. An early problem was the shipboard custom of frequently painting parts of the ship. When submarines were found to have very heavy hydrocarbon loads in the main adsorbent bed after painting (9,13), and when the organic contaminant distribution was shown to approximate the solvent mixture in military paints and diesel fuels (10), thought was given to disallowing painting on patrol. NRL worked on formulating a low-solvent, but fire-resistant paint (8). Painting was prohibited 5 days before and during deployment. In addition, adhesives for decorative and insulating paneling were found to emit solvents for months after application (25).

Halogenated compounds have also been a problem. Refrigerants R-11 or R-114, and R-12 have been used in submarine freezers and air conditioning units. Refrigerant R-113 is used (not at sea) for cleaning both submarine and diving gear. Methyl chloroform is a component of many adhesives, including ones used for fastening interior paneling in submarines (25). These compounds are not usually a direct problem because of their relatively low toxicity, but rare large volume liquid spills (7) and many smaller ones (31) can put substantial quantities of these chemicals into the submarine atmosphere. "Normal" levels of these compounds vary drastically among submarines and between patrols in the same submarine (35). Greater concern arises from the interaction of these compounds in the atmosphere control equipment. Both R-11 and methyl chloroform decompose in the CO-H₂ catalytic burner to form hydrogen fluoride (HF), hydrochloric acid (HCl), vinylidene chloride, and monochloroacetylene; all are dangerous compounds (16). Decomposition also can occur on LiOH scrubbers used for CO₂ removal (33). Previous use of trichloroethylene which decomposes into the extremely toxic dichloroacetylene (28), is now avoided by a prohibition on using that solvent.

A very large number of hydrocarbons have been found (6). Sources include volatile industrial products, food and cooking, and human waste.

These range from short, relatively harmless, aliphatics to many troublesome derivatives of benzene (10). Since the aromatic fractions were found to be similar to paint formulations now outmoded, that source may now be less important. Toluene, however, is a very common solvent in many industrial applications. Venting of the emergency diesel fuel tanks results in another likely source of both aliphatic and aromatic compounds. A recurring fraction of aliphatics, the C-9 to C-13 alkanes, appears to arise from oil lubricants in on-board machinery (36). Assessment of the hydrocarbon problem is hindered by the dearth of data on contaminant distribution in submarine atmospheres reported in the last 15 years.

Sources exist for inorganic gases. A high voltage electrostatic precipitator has been known to produce ozone, and many other pieces of electrical equipment with ionizing voltages are in use. Ozone is relatively unstable and is unlikely to survive the compression and piping necessary to deliver gas to divers. The acid gases NO_2 and SO_2 can arise from any combustion process, such as catalytic oxidation of diesel or torpedo fuel (15) and operation of the standby diesel engine (3), but these gases are also unlikely to survive the passage to divers. Ammonia can arise from degradation of monoethanolamine scrubbing solution.

Since successful decontamination is very difficult to achieve, a program of elimination of source material has been developed. A Navy laboratory has tested bulk and offgassing components of several hundred commercial substances which were then placed in categories as to allowable presence and use (6). For example, this approach led to the prohibition of floor polishes containing mercury (24). Unfortunately the testing program cannot match the demand for use of new products, and stories abound of how the rules are ignored or circumvented.

Very little recent data exists on the distribution of atmosphere contaminants. In the following sections, we will present the results of a poll of operating submarines and some laboratory analyses of diving air from actual submarine operations.

DETECTOR TUBE SURVEY OF ATLANTIC FLEET SSNs

Background and Methods

One of the very few ways that the distribution of submarine atmosphere trace contaminants has been sampled is by use of detector tubes. These are sealed glass vials containing chemical reagents and colorometric indicator substances that develop a stain the length of which is dependent on contaminant concentration in a stream of air. When submerged, the Submarine Atmosphere Control Manual (17) requires a battery of samples to be performed at least weekly. The tubes carried on-board, their minimum detectable concentration, and some of the interfering substances are provided in Table 1. Note that many tubes have cross reactivity, at least at high concentration. The apparent redundancy of hydrazine and ammonia tubes results from different administrative requirements.

In the Summer of 1985, a request was made to Atlantic Fleet nuclear attack submarines to examine their detector tube readings over the last year, report both average and maximum values, and document any other indications of atmospheric problems. Thirty-four submarines replied; 2 provided no data. Most averages were based on 10-20 rounds of samples, but 2 boats averaged over 100 sets of readings.

Results

Table 2 presents reported average concentrations, and Table 3 has the reported maximum readings. A number of problems decreased the value of these reports. Missing, inconsistent, or incorrect units of measurements were fairly common (many of the CO₂ entries labelled N in the tables are from reports of CO₂ at a few ppm). A few average values greater than highest values were reported. When lowest detectable units were given, some reports had values that corresponded to neither the manufacturer's package insert nor to the Submarines Atmosphere Control Manual. There is no assurance that each boat pushed the sensitivity of the tubes to the minimum detectable values in Table 1. Presumably, these problems are a combination of limited training of the corpsmen responsible for monitoring, limited care in performing and

transcribing the tests, and possible inconsistencies in the Federal Supply System that buys and stocks tubes for submarine use. We have attempted to remove obviously erroneous entries from the tables.

Overall, it is obvious that the atmospheres are relatively free of contaminants at the sensitivity level of these tubes. No submarines reported any detectable benzene or sulfur dioxide. Chlorine, ozone and 1,1,1-trichloroethane (methyl chloroform) were each reported by only a single boat. Acetone, hydrochloric acid, toluene, and nitrogen dioxide were also rare. Ammonia and/or hydrazine incidents were fairly common. The high hydrazine levels reported by boats 17 and 18 were said to be traced to spillage of monothalamine from the scrubber units. The failure of ammonia and hydrazine reports to be coincident as expected by their cross-sensitivity is puzzling.

As expected, both CO and CO₂ are detected frequently by detector tubes. Both compounds are monitored continuously by the boat's CAMS-I. Because only occasional violations occur during the 90-day patrol limits for these compounds (0.8% CO₂, 15 ppm CO), it appears that the atmosphere control equipment works rather well. One submarine (No. 11) reported an average trichloroethylene level of 50 ppm by an unspecified analysis. Included in reports from boats 1 and 16 were references to refrigerant leaks that raised local R-12 levels to several hundred ppm (measured by CAMS-I). Contrary to expectation, contaminants did not show a clear improvement in newer submarines (boats 1, 19, 21, 22, and 25 are over 25 years old; 3, 13, 16, 18, and 29 are less than 7 years old).

ANALYSIS OF RECENT DRY DECK SHELTER GAS

Background and Methods

Most diving from submarines has been of a small enough scale to allow divers to breathe from SCUBA tanks carried on-board by themselves or from air banks filled with fresh air before the submarine submerged. A new operation called the Dry Deck Shelter (DDS) program, uses enough air to make reliance on the ship's normal air banks necessary. During the Fall of 1985 and Winter of

1986, people working on the DDS program cooperated with this laboratory in getting a series of gas samples for analysis. All data came from a single submarine. Because gas data recording was a low priority task for the people on-board, details of the history of the samples is scanty. In particular, we do not know which submarine air banks were filled from fresh air or from recirculated submarine air and how long since submergence were any of the samples taken. We also do not know which samples were obtained downstream of a LiOH scrubber unit installed to remove CO₂ before use by the divers.

Gas samples were taken from the submarine's air banks in 500 ml stainless steel cylinders (Whitney model 67), which were pressure-rated at 1800 psi but usually filled to 100-500 psi. Cylinders were cleaned and evacuated to 30 mTorr before shipment to the submarine. The few cylinders that arrived in the lab without positive pressure were not analyzed. Connection to the ship's banks were made with stainless steel whips that had previously been certified as clean.

In the laboratory, samples were withdrawn for analysis from the cylinders via a high-purity, low-flow 2-stage regulator after a 4-cycle purge procedure had been completed with the regulator. Carbon dioxide and O₂ analysis was performed with a Sigma-4 isothermic gas chromatograph (Perkin Elmer) using a gas sample valve and a column reversal procedure on molecular sieve 5A and Chromosorb 102 (Supelco) packing. Hydrocarbon analysis was performed on a Shimadzu GC-9A temperature programmable gas chromatograph using either a gas sampling valve or direct injection with gas-tight syringe. A methyl silicone (SP-2100, Supelco) packed column and a temperature ramp of 50 to 100 °C were used. Low boiling components were chromatographed on a 3% SP-1500 on Carbopack-B (Supelco) column. In some cases, unknown peaks were identified with a Hewlett Packard 5970B Mass Selective Detector using a 0.75 mm ID capillary column and library software. All instruments were calibrated using gravimetric standards certified to ±2% of stated value (Scott Specialty Gases). Normal calibration gases were benzene, toluene, xylenes, methyl chloroform and R-113 for hydrocarbons (about 10 ppm each); R-11, R-12, R-22,

R-114, methane, ethane, propane, butane, pentane, and hexane for low boiling separations (each at about 10 ppm). Laboratory reproducibility of retention times is <0.3 sec SD and of peak areas is <2% SD. Low limits of detection are in the range of 0.05-0.5 ppm for the calibration gases, and a single sensitivity limit of 0.5 ppm is presumed for the unknowns reported in Table 4. Some samples were analyzed for CO by an infrared spectrometer (Beckman 865) with a 15 inch gas cell pressurized to 10 to 50 psig.

Analytical Results

Data for 11 known compounds are presented in Table 4 according to sample date and the submarine air bank used. Other compounds found, but not yet identified, are included in the table as unknowns. O₂ (plus argon) was quite constant with all readings between 20 and 22%. CO₂ was extremely variable, spanning a 60-fold range. The lowest readings were probably downstream of the DDS special LiOH scrubber since submarine atmospheres almost always contain at least 0.03% CO₂. The highest CO₂ readings would be of real concern for diving. Only a few samples were analyzed for CO since our instrument required large quantities of gas for purging the optical cell. The few CO readings obtained did not indicate a substantial hazard.

Low boiling point aliphatic hydrocarbons were prevalent. Methane was present in all samples at levels of 2-12 ppm. These levels raise no toxicity problems. The C-2 to C-6 alkanes (ethane through hexane) were seen less often, with a tendency of concentration to decrease as the size increase. The instruments were not calibrated with higher alkanes, which would evaporate from fuels and lubricant oils. Nevertheless, the procedures employed would have detected the C-7 to C-14 alkanes in those fuels at efficiencies similar to the other alkanes, which have a sensitivity of about 0.1 ppm.

Halogenated compounds were found in all samples. The low and fairly constant levels (0.5 to 14 ppm) of R-12 and R-114 probably arose from slow leaks in the submarine's air conditioning systems. The absence of these compounds in the earlier samples (Summer of 1985; unreported) may be due to special bank purging procedures, but may also be an analytical artifact.

These samples were stored in sample bombs for about a year before analysis was complete. Gas sample storage for this duration is possible in carefully prepared standards (29) and tests on similar submarine sampling equipment showed stability for 3 months (30). Note the day-to-day variability of over 7-fold for R-114 in air bank 5.

Many compounds of concern were not detected in these samples (see note 3 in Table 4). These included aromatics and halogenated compounds that gave rise to toxicity questions in the past. Specifically not detected were compounds reported (by detector tube) to be recently present on other submarines such as toluene and trichloroethane. On the other hand, several other substances were found but not identified (see note 6 in Table 4). These occasional contaminants may become known in the future, but now serve as a reminder that no gas analysis is "complete." Overall, the analyses indicate that the atmospheres in these submarine banks (except CO₂) were well below the contaminant levels required by present guidelines.

CONCLUSION

This report is the first step toward development of a purity standard and method of analysis that can be used in support of diving operations from submarines. The severe boat to boat variability seen in detector tube results (Tables 2 and 3) makes an "average" analysis useless for setting a standard. Additional samples will be required to see what contaminants occur with any regularity. The numerous questions on data quality from the exercise with detector tubes is a warning that any new procedure will need to be suitable for people who lack skills in analytical chemistry. Likewise, the day-to-day variability of air in a single submarine makes it important to allow frequent repetitive analyses. The semi-annual check of air banks required by the Diving Manual (18) is not sufficient to ensure diver safety.

Further steps in developing a practical standard can be outlined. Analytical capabilities will be increased by using absorption concentration to increase sensitivity, and by using mass spectrometer identification procedures

to increase specificity. These requirements are also needed for full monitoring of a human pressure chamber (34). Both abilities will be required to investigate whether any toxic compounds normally in the 1-100 ppb range are present. There is a need to increase the number and frequency of boats examined. As the picture of contaminant profiles sharpens, there will be a need to evaluate critically the compounds for maximum plausible toxic risk and to evaluate appropriate on-board analysis procedures. Interim answers in this regard have just recently been issued (19).

REFERENCES

1. Alexander AL and VR Piatt, eds. Fifth annual progress report. The present status of chemical research in atmosphere purification and control on nuclear powered submarines. Naval Research Laboratory Report 6491 Jan 1967.
2. Bondi KR. Current submarine carbon monoxide and estimated carboxyhemoglobin levels and interpretation of their possible effects on mental health and performance. Groton, CT: Naval Submarine Medical Research Lab Report 883, Nov 1978 (NTIS AD-A063274).
3. Bondi KR, ML Shea, and RM DeBell. Nitrogen dioxide levels aboard nuclear submarines. American Industrial Hygiene Association Journal, Vol. 44, pp. 828-832, 1983.
4. Carhart HW and Piatt VR, eds. Third annual progress report. The present status of chemical research in atmosphere purification and control on nuclear powered submarines. Naval Research Laboratory report 6053, Dec 1963.
5. DeCorpo JJ, JR Wyatt, and FE Saalfeld. Central Atmosphere Monitor (CAMS). Naval Engineering Journal, Vol. 92, pp. 231-238, 1980.
6. Demas P and M Greenberg. Manual of procedures for chemical analyses of materials used in nuclear submarines. Bethesda, MD: David W. Taylor Naval Ship Research and Development Center. Report (Draft) DTNSRDC/SME-86/24, April 1986.
7. Eaton HG. Measurement and removal of Freon-TF from a submarine atmosphere. Report of trip to USS Salmon (SS-573). Naval Research Laboratory Report 2182, Nov 1970.
8. Eaton HG, FW Williams, PA Tatem. Combustion products evaluation from hull insulation materials coated with fire retardant paints. Naval Research Laboratory Report 8403, Sept 1980 (NTIS AD-A089973).

9. Herrmann EM. Atmosphere monitoring in nuclear powered submarines. Annapolis, MD: United States Navy Marine Engineering Laboratory Report 73 111, Aug 1963.
10. Johnson JE, AJ Chiantella, WD Smith, and ME Umstead. Nuclear submarine atmospheres. Part 3 - Aromatic content. Naval Research Laboratory Report 6131, Aug 1964.
11. Knight DR and KR Bondi. Proceedings of the Third Tripartite Conference on Submarine Medicine. Groton, CT: Naval Submarine Medical Research Laboratory. Special Report 83-1, June 1983.
12. Lockhart LB and VR Piatt, eds. Fourth annual progress report. The present status of chemical research in atmosphere purification and control on nuclear-powered submarines. Naval Research Laboratory Report 6251, Mar 1965 (NTIS AD-614261).
13. MaxNestler FH and WD Smith. Submarine habitability-atmosphere sampling and analysis. Naval Research Laboratory Memo Report 866, Oct 1958.
14. Miller RR and VR Piatt, eds. Sixth annual progress report. The present status of chemical research in atmosphere purification and control on nuclear powered submarines. Naval Research Laboratory Report 6722, June 1968 (NTIS AD-837300).
15. Musick JK and JE Johnson. The interaction of Otto fuel with the atmosphere control systems used in nuclear submarines. Naval Research Laboratory Report 6642, Dec 1967 (NTIS AD-825399).
16. Musick JK, FW Williams, and JE Johnson. Reactions of halogenated hydrocarbons in the acid scrubber of the Mark V CO/H₂ burner [Confidential rep, UNCLASS title]. Naval Research Laboratory Report 8011, Oct 1976.
17. Naval Sea Systems Command. Submarine Atmosphere Control Manual. U.S. Navy. S9510-AB-ATM-010/(C) SUB ATM CONT, 1979.

18. Naval Sea Systems Command. U.S. Navy Diving Manual. Vol. 1, Air Diving. NAVSEA 0994-LP-001-9010. Washington, DC: U.S. Government Printing Office, 1985.
19. Naval Sea Systems Command. Interim air purity guidelines for dry deck shelter operations. Letter 10560, Ser 00C3/2101, 16 July 1986.
20. Piatt VR and EA Ramskill. Progress report: Chemical research in nuclear submarine atmosphere purification. Naval Research Laboratory Report 7037, June 1970 (NTIS AD-709896).
21. Piatt VR and EA Ramskill, eds. Annual progress report. The present status of chemical research in atmosphere purification and control on nuclear-powered submarines. Naval Research Laboratory Report 5630, July 1961 (NTIS AD-260235).
22. Piatt VR and JC White, eds. Second annual progress report. The present status of chemical research in atmosphere control on nuclear-powered submarines. Naval Research Laboratory Report 5814, Aug 1962 (NTIS AD-284576).
23. Pustinger JV, FN Hodgson, JE Strobel, and R Evers. Identification of volatile contaminants of space cabin materials. Dayton, OH: Aerospace Medical Research Laboratory. Report AMRL 69-71, 1969.
24. Ross PH. Analysis of hotel and personal materials used aboard operating submarines. U.S. Navy Marine Engineering Lab Report MEL 40/67 1967 (NTIS AD-806974).
25. Saalfeld FE and MV McDowell. Diffusion rates of methyl chloroform through some insulation materials. Naval Research Laboratory Report 6302, July 1965.
26. Saalfeld FE and RA Saunders. Analysis of encapsulated environments. In: Mass Spectrometry, Part A. Merrit C and CN McEwen, eds. Dekker, NY, 1979, pp. 119-144.

27. Saalfeld FE and JR Wyatt. NRL's central atmosphere monitor program. Naval Research Laboratory Memo Report 3432, Dec 1976 (NTIS AD-A035774).
28. Saunders RA. A new hazard in closed environmental atmospheres. Archives of Environmental Health, Vol. 14, pp. 380-384, 1967.
29. Schmidt WP and HL Rook. Preparation of gas cylinder standards for the measurement of trace levels of benzene and tetrachloroethylene. Analytical Chemistry, Vol. 55, pp. 290-294, 1983.
30. Smith DE and TL King. A statistical study of grab sampling in a closed environment. Desmatics, Inc. (State College, PA) Tech Report 106-4, Feb 1977.
31. Smith WD, FJ Woods, and ME Umstead. Submarine atmosphere studies aboard the USS Scamp. Naval Research Laboratory Report 6312, Oct 1965 (NTIS AD-1474373).
32. Spain D, JJ DeCorpo, and JR Holtzclaw. Use of a photoionization detector as a hydrocarbon trace gas analyzer. Naval Research Laboratory Memorandum Report 4239, 1980.
33. Spain MA, BS Middleditch, DA Bafus, and T Galem. Dehydrohalogenation of atmospheric contaminants in the space cabin. Aviation, Space and Environmental Medicine, Vol. 56, pp. 262-264, 1985.
34. Weathersby PK, RS Lillo, ET Flynn, JR Wyatt, and WD Dorko. Trace chemical contaminants in a new human pressure chamber. Bethesda, MD: Naval Medical Research Institute Technical Report No. 86-54, 1986.
35. William FW and JE Johnson. Halogenated hydrocarbons in the atmospheres of submarines in squadron fifteen. Naval Research Laboratory Report 6708, June 1968 (NTIS AD-392471).
36. Wyatt. Personal communication, 1986.

Table 1
Detector tubes required on submarines.

<u>Contaminant</u>	<u>Minimum Detectable</u>		<u>Interferences</u>
CO(CH ₃) ₂ CH 22901	Acetone	100 ppm	Other ketones, ammonia
NH ₃ CH 20501	Ammonia	1.0 ppm*	Hydrazine, other organic bases
C ₆ H ₆ CH 24801	Benzene	15 ppm	Compounds resistant to pre-treatment with acid, aldehyde
CO ₂ CH 23501	Carbon dioxide	0.1%*	None (hydrazine reaction)
CO CH 20601	Carbon monoxide	10 ppm*	Acetylene, other hydrocarbons
Cl ₂ CH 23401	Chlorine	0.2 ppm*	Br ₂ , ClO ₂ , NO ₂
N ₂ H ₄ CH 31801	Hydrazine	0.25 ppm	NH ₃ , amines
HCl CH 29501	Hydrochloric acid	0.1 ppm*	Cl ₂
NO ₂ CH 30001	Nitrogen dioxide	0.1 ppm*	O ₃ , Cl ₂
O ₃ CH 31301	Ozone	0.005 ppm*	Cl ₂ , NO ₂
SO ₂ CH31701	Sulfur Dioxide	1 ppm	NO ₂
C ₆ H ₅ CH ₃ CH 27801	Toluene	25 ppm	Xylenes, ethylbenzene, cumene
Total Hydrocarbon CH 23001 (Toluene 5/a)		60 mg/m ³	Qualitative
CH ₃ CCl ₃ CH 21101	1,1,1-trichloroethane	50 ppm	Other chlorocarbons

- Notes:
1. Under each chemical is the serial number of the tube; all manufactured by Dragerwerk AD, Lubeck, W. Germany.
 2. Entries with '*' are the greatest sensitivity stated by the manufacturer; less sensitive scales are also present.
 3. The total hydrocarbon entry uses a "toluene" tube. Its iodine pentoxide reaction to liberate iodine is susceptible to many aliphatic and aromatic hydrocarbons, hence the label of "total hydrocarbon."

Table 2

Average reported levels (ppm except CO₂) on submarines determined by detector tubes.

Submarine	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10	#11	#12	#13	#14	#15	#16	#17
Contaminant																	
ACETONE, ppm	L	<300	L	L	L	L	L	L	L	L	N	L	N	L	L	L	L
AMMONIA, ppm	1.0	<25	L	L	L	L	L	L	L	L	7	L	<5	L	L	L	<5
BENZENE, ppm	L	N	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L
CARBON DIOXIDE, %	0.5	0.6	0.3	0.5	0.1	0.5	0.6	0.4	0.5	0.4	0.3	0.6	0.5	0.2	N	0.5	N
CARBON MONOXIDE, ppm	8	6	4	L	L	2	L	L	3	5	11	L	L	L	L	4	L
CHLORINE, ppm	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L
HYDRAZINE, ppm	0.5	N	L	0.3	0.1	0.1	L	L	L	0.1	L	L	L	L	L	L	0.2
HYDROCHLORIC ACID, ppm	L	N	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L
NITROGEN DIOXIDE, ppm	L	<.5	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L
OZONE, ppm	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L
SULFUR DIOXIDE, ppm	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L
TOLUENE, ppm	N	<50	L	L	L	N	L	L	L	L	N	L	L	L	L	L	L
THC, qualitative	L	N	L	L	L	L	L	L	L	L	N	L	L	L	L	L	L
TRICHLORO-ETHANE, ppm	L	N	L	L	L	L	N	L	L	L	50	L	L	L	L	L	N

Notes:

1. Entries of 'L' are made when reported value was less than manufacturers reported minimum sensitivity, cf., Table 1.
2. Entries of 'N' are made when measurement was not made, not reported, or reported clearly in error.

Table 2 (continued)

Submarine	#18	#19	#20	#21	#22	#23	#24	#25	#26	#27	#28	#29	#30	#31	#32	#33	#34
Contaminant																	
ACETONE, ppm	L	L		L	L		L	L	L	L	L	L	L	L	L	L	L
AMMONIA, ppm	L	0.7		1	L		L	4.0	L	L	1.4	L	L	L	1.0	L	L
BENZENE, ppm	L	L		L	L		L	L	L	L	L	N	L	L	L	L	L
CARBON DIOXIDE, %	N	0.6		0.6	N		0.5	N	0.8	0.3	0.5	0.7	0.4	0.2	0.5	0.8	0.3
CARBON MONOXIDE, ppm	N	6		4	0.6		0.8	4	0.7	N	2.5	5	L	L	2	N	<0.5
CHLORINE, ppm	L	L		L	L		L	L	L	L	L	L	L	L	L	L	L
HYDRAZINE, ppm	L	0.6		<0.5	N		0.1	L	L	L	L	N	L	L	0.8	L	L
HYDROCHLORIC ACID, ppm	L	L		L	L		L	L	L	L	L	L	L	L	L	L	L
NITROGEN DIOXIDE, ppm	L	L		L	L		L	L	L	L	L	N	L	L	L	L	L
OZONE, ppm	L	L		L	L		L	L	L	L	L	L	L	L	L	L	L
SULFUR DIOXIDE, ppm	L	L		L	L		L	L	L	L	L	L	L	L	L	L	L
TOLUENE, ppm	L	L		L	L		L	L	L	L	L	L	L	L	L	L	L
THC, qualitative	L	L		N	N		L	L	L	L	L	N	L	L	L	L	L
TRICHLORO- ETHANE, ppm	L	L		N	L		L	L	L	L	L	N	L	L	L	L	L

Notes:

1. Entries of 'L' are made when reported value was less than manufacturers reported minimum sensitivity, cf., Table 1.
2. Entries of 'N' are made when measurement was not made, not reported, or reported clearly in error.

Table 3

Maximum reported levels (ppm except CO₂) on submarines determined by detector tubes.

Submarine	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10	#11	#12	#13	#14	#15	#16	#17
Contaminant																	
ACETONE, ppm	L	<300	L	N	L	L	L	L	L	L	N	L	N	L	L	L	N
AMMONIA, ppm	2.5	<25	L	5	1	L	L	L	L	L	25	L	<5	L	L	L	<5
BENZENE, ppm	L	N	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L
CARBON DIOXIDE, %	1.0	0.8	0.5	0.8	0.1	0.8	1.0	0.5	0.7	0.8	0.6	0.7	0.6	0.2	N	0.9	N
CARBON MONOXIDE, ppm	13	10	8	L	L	7	L	L	5	15	15	L	L	L	L	7	L
CHLORINE, ppm	L	L	L	0.2	L	L	L	L	L	L	L	L	L	L	L	L	L
HYDRAZINE, ppm	2.2	N	L	1	0.3	0.3	L	L	L	0.5	L	L	.25	L	L	L	2
HYDROCHLORIC ACID, ppm	L	N	L	L	L	L	L	L	L	L	L	L	<1	L	L	L	9
NITROGEN DIOXIDE, ppm	L	<0.5	L	L	L	L	L	L	L	L	L	L	<0.5	L	L	L	<0.5
OZONE, ppm	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L	<0.05
SULFUR DIOXIDE, ppm	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L
TOLUENE, ppm	N	<50	L	L	L	N	L	L	L	25	N	L	L	L	L	L	L
THC, qualitative	L	N	L	L	L	L	L	L	+	L	N	L	L	L	L	L	L
TRICHLORO-ETHANE, ppm	L	N	L	L	L	L	N	L	L	L	50	L	L	L	L	L	N

Notes:

1. Entries of 'L' are made when reported value was less than manufacturers reported minimum sensitivity, cf., Table 1.
2. Entries of 'N' are made when measurement was not made, not reported, or reported clearly in error.
3. CO entries less than the 10 ppm in Table 1 were provided, presumably from the CAMS-I.
4. +: positive indication of hydrocarbons.

Table 3 (continued)

Submarine	#18	#19	#20	#21	#22	#23	#24	#25	#26	#27	#28	#29	#30	#31	#32	#33	#34
Contaminant																	
ACETONE, ppm	L	L		L	L		L	0.1	L	L	L	L	L	L	L	L	L
AMMONIA, ppm	L	5		2	L		L	22	L	L	5	L	L	L	5	L	L
BENZENE, ppm	L	L		L	L		L	L	L	L	L	N	L	L	L	L	L
CARBON DIOXIDE, %	N	2.0		0.7	N		0.7	N	1.1	0.4	0.7	1.0	0.6	0.4	0.8	1.0	0.4
CARBON MONOXIDE, ppm	N	11		7	2.2		10	8	2	N	5	12	L	L	5	N	<0.5
CHLORINE, ppm	L	L		L	L		L	L	L	L	L	L	L	L	L	L	L
HYDRAZINE, ppm	0.15	2		<0.5	N		0.3	L	L	L	1	N	0.3	L	2.5	L	L
HYDROCHLORIC ACID, ppm	L	L		L	L		L	L	L	L	L	L	L	L	L	L	L
NITROGEN DIOXIDE, ppm	L	L		L	L		L	L	L	L	L	N	L	L	L	L	L
OZONE, ppm	L	L		L	L		L	L	L	L	L	L	L	L	L	L	L
SULFUR DIOXIDE, ppm	L	L		L	L		L	L	L	L	L	L	L	L	L	L	L
TOLUENE, ppm	L	L		L	L		L	L	L	L	L	L	L	L	L	L	L
THC, qualitative	L	L		N	N		L	L	L	L	L	N	L	L	L	L	L
TRICHLORO-ETHANE, ppm	L	L		N	L		L	L	L	L	L	N	L	L	L	L	L

Notes:

1. Entries of 'L' are made when reported value was less than manufacturers reported minimum sensitivity, cf., Table 1.
2. Entries of 'N' are made when measurement was not made, not reported, or reported clearly in error.
3. CO entries less than the 10 ppm in Table 1 were provided, presumably from the CAMS-I.

Table 4

Gas analysis results from one submarine (% for O₂, CO₂; ppm for others).

<u>Air Bank</u>	<u>Date</u>	<u>CO₂</u>	<u>O₂*</u>	<u>CO</u>	<u>Methane</u>	<u>Ethane</u>	<u>Propane</u>	<u>Pentane</u>	<u>Hexane</u>	<u>R-12</u>	<u>R-113</u>	<u>R-114</u>	<u>Unknowns</u>
1	?	0.03	22.0	-	2.1	<0.05	?	<0.05	<0.05	?	<0.1	?	1?
	11/10/85	0.02	20.8	-	9.0	0.15	0.06	<0.05	<0.05	5.8	<0.1	4.1	1
	14/02/86	0.15	21.7	1.2	2.8	<0.05	<0.05	<0.05	<0.05	2.1	<0.1	2.4	N
	22/02/86	<0.01	21.6	-	4.0	0.06	<0.05	<0.05	<0.05	2.5	<0.1	2.9	1
2	?	0.03	21.8	-	2.0	<0.05	<0.05	<0.05	<0.05	0.5	<0.1	<0.1	N
	11/10/85	0.15	21.6	-	5.0	0.09	<0.05	<0.05	<0.05	3.8	0.3	2.2	1,2
	16/10/85	0.07	21.7	-	3.1	<0.05	<0.05	<0.05	<0.05	1.5	<0.1	2.0	1,3
3	?	0.04	21.9	-	2.1	<0.05	<0.05	<0.05	<0.05	<0.2	<0.1	<0.1	N
	13/10/85	0.05	21.4	-	6.9	0.12	<0.05	<0.05	<0.05	4.9	<0.1	4.4	1
	15/10/85	0.13	21.4	-	6.7	0.11	<0.05	<0.05	<0.05	4.8	<0.1	4.2	1
	14/02/86	0.19	21.7	-	3.7	<0.05	<0.05	<0.05	<0.05	3.2	<0.1	3.1	1
4	?	0.06	21.9	-	2.0	<0.05	<0.05	<0.05	<0.05	0.5	<0.1	<0.1	N
	14/02/86	0.21	21.5	1.2	3.5	<0.05	<0.05	<0.05	<0.05	3.8	<0.1	3.2	1

Table 4 (continued)

<u>Air Bank</u>	<u>Date</u>	<u>CO₂</u>	<u>O₂*</u>	<u>CO</u>	<u>Methane</u>	<u>Ethane</u>	<u>Propane</u>	<u>Pentane</u>	<u>Hexane</u>	<u>R-12</u>	<u>R-113</u>	<u>R-114</u>	<u>Unknowns</u>
5	?	0.07	21.8	-	2.0	?	?	<0.05	<0.05	?	?	?	1
	14/02/86	0.19	21.6	1.3	3.4	<0.05	<0.05	<0.05	<0.05	3.2	<0.1	2.8	1
	15/02/86	<0.01	21.7	2.9	3.0	<0.05	<0.05	<0.05	<0.05	2.3	<0.1	1.8	3
	18/02/86	<0.01	21.4	-	4.7	0.08	<0.05	<0.05	<0.05	3.2	<0.1	3.7	1
	24/02/86	0.03	21.4	-	5.5	0.08	<0.05	<0.05	<0.05	5.4	<0.1	2.7	1,3
	26/02/86	<0.01	21.2	-	5.3	0.08	<0.05	<0.05	<0.05	4.6	<0.1	3.6	1,3
	04/03/86	0.39	21.4	-	8.1	0.13	0.05	0.12	0.13	8.4	<0.1	10.0	1,2,3
	05/03/86	0.59	20.0	-	11.8	0.18	0.05	<0.05	<0.05	12.0	<0.1	14.2	1,2,3

Notes:

1. CO₂ and O₂ values are percent; all other values are ppm.
2. * O₂ analysis includes Ar in addition to O₂.
3. None of the samples showed the following compounds at levels greater than the limits of detectability (ppm) given:

1,1,1-Trichloroethane: 0.5

Benzene: 0.1

Toluene: 0.1

m-,p-Xylene (combined): 0.1

o-Xylene: 0.1

R-11: 0.5

R-22: 0.5

Table 4 (continued)

n-Butane	Retention time of optical isomer of R-114 coincided with that of butane so information on butane not available.
4. ? under amount:	indicates possible amount above the level of detectability but sample loss prevented quantification.
? under data:	exact sample date unknown, Summer of 1985.
5. -:	indicates analysis for CO not performed.
6. Unknowns:	reported if above the level of detectability of methane after assuming response equivalent to methane.
	#1, retention time between methane and ethane
	#2, retention time between R-22 and propane
	#3, retention time between R-12 and R-114
	#?, indicates possible amount above the level of detectability but sample loss prevented quantification.
	N, none detected